

# Naval Surface Warfare Center Carderock Division

Bethesda, MD 20084-5000

---

NSWCCARDIV-TR-96/003 March 1996

Survivability, Structures, and Materials Directorate

Technical Report

## Testing Lithium/Carbon Monofluoride Batteries for Naval Applications

by

Glenn Zoski

Advanced Technology and Research Corporation

19971103 097



DTIC QUALITY INSPECTED 3

---

Approved for public release; distribution is unlimited.

---

**Naval Surface Warfare Center  
Carderock Division**

Bethesda, MD 20084-5000

---

**NSWCCARDIV-TR-96/003 March 1996**

Survivability, Structures, and Materials Directorate

Technical Report

**Testing Lithium/Carbon Monofluoride Batteries for  
Naval Applications**

by

Glenn Zoski

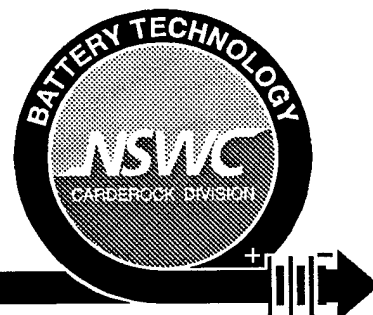
Advanced Technology and Research Corporation

---

Approved for public release; distribution is unlimited.

---

DTIC QUALITY INSPECTED 3



# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 1996	3. REPORT TYPE AND DATES COVERED Final; June 1992 to February 1994	
4. TITLE AND SUBTITLE Testing Lithium/Carbon Monofluoride Batteries for Naval Applications			5. FUNDING NUMBERS	
6. AUTHOR(S) Glenn Zoski				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Advanced Technology and Research Corporation 15210 Dino Drive Burtonsville, MD 20866-1172			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Surface Warfare Center Carderock Division, White Oak Laboratory 10901 New Hampshire Ave. Silver Spring, MD 20903-5640			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NSWCCARDIV-TR-96/003	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  This investigation was part of a continuing effort to identify or develop battery technology having higher voltage, good rate capability, improved safety, cost effectiveness and easy disposal. Perceived safety risks and storage problems have limited use of lithium batteries by the Navy. This study evaluated the performance of Panasonic Model BR-C lithium/carbon monofluoride batteries over a wide temperature range. Battery rate limitation and the discharge mechanism were also investigated. Four sets of batteries, three batteries per set, were discharged at temperatures of -20°C, 0°C, 25°C and 70°C respectively. The batteries were discharged under constant load conditions of 5 and 50 ohms. Environmental chambers were used to maintain temperature control. Performance at room temperature and above was quite good and the reproducibility of the battery discharge behavior was excellent. Low temperature performance was poor, especially at the higher discharge rate. An unexplained temperature excursion occurred on batteries discharged at -20°C, raising a potential safety concern. A better understanding of the discharge mechanism requires collection of impedance data throughout the discharge process. The effects of the spirally-wound construction could be accounted for if a prismatic version of the LiCFx battery were constructed and used for the impedance measurements.				
14. SUBJECT TERMS batteries                      lithium batteries			15. NUMBER OF PAGES 25	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 3  
i/ii

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

**Contents**

	Page
<b>Figures</b> .....	iv
<b>Tables</b> .....	iv
<b>Preface</b> .....	v
<b>Introduction</b> .....	1
<b>Experimental</b> .....	1
Cell Construction .....	1
Test Equipment .....	2
Cycling and AC Impedance Procedures .....	2
<b>Results and Discussion</b> .....	2
Discharge Behavior .....	3
Impedance Spectroscopy .....	6
<b>Conclusions</b> .....	7
<b>Recommendations</b> .....	8
<b>References</b> .....	18
<b>Initial Distribution</b> .....	(1)

### Figures

	Page
1 Discharge Curve for Three Cells under a Load of 50 ohms at 70°C.....	9
2 Discharge Curve for Three Cells under a Load of 50 ohms at 25°C.....	9
3 Discharge Curve for Three Cells under a Load of 50 ohms at 0°C.....	10
4 Discharge Curve for Three Cells under a Load of 50 ohms at -20°C.....	10
5 Discharge Curve for Three Cells under a Load of 5 ohms at 70°C.....	11
6 Discharge Curve for Three Cells under a Load of 5 ohms at 25°C.....	11
7 Discharge Curve for Three Cells under a Load of 5 ohms at 0°C.....	12
8 Discharge Curve for Three Cells under a Load of 5 ohms at -20°C.....	12
9 Complex Plane Impedance Spectra for Three Fresh Cells Prior to Discharge.....	13
10 Complex Plane Impedance Spectra for Two Cells Completely Discharged with a 50-ohm Load .....	13
11 Equivalent Circuit Used to Model a Diffusional Impedance and the Observed Impedance within a Porous Structure .....	14
12 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 50 ohms at 0°C .....	14
13 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 50 ohms at -20°C .....	15
14 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 70°C .....	15
15 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 25°C .....	16
16 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 0°C .....	16
17 Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at -20°C.....	17

### Table

1 Average Plateau Voltage and Average Capacity.....	3
---	---

### **Preface**

This investigation is part of a continuing effort to characterize available battery systems for potential use in many present and new naval applications. The initial investigation addressed the temperature range over which the commercially available lithium carbon monofluoride batteries could be used. Impedance spectroscopy was applied in an effort to provide insight into the rate limitation and the discharge mechanism.

This work was sponsored by Office of Naval Research under the High Energy Battery Project, and directed by Dr. Patricia H. Smith at the Naval Surface Warfare Center, Carderock Division (NSWCCD), White Oak Detachment. The work was performed by Advanced Technology and Research (ATR) Corporation of Burtonsville, Maryland, under contract N60921-92-D-0002.

The authors wish to acknowledge the numerous and helpful scientific discussions with Dr. Charles Fleischmann of ATR.

### Introduction

This investigation is part of a continuing effort to characterize and evaluate available battery systems for potential use in present and new naval applications. Navy use of lithium batteries has been limited because of the perceived safety risks and storage problems associated with higher energy density chemistries such as lithium/thionyl chloride. Nevertheless, the higher voltage available with the lithium systems is very attractive. Consequently, there is an ongoing effort to improve existing lithium chemistries or find new ones. The goals are to provide higher voltage, good rate capability, safety, cost effectiveness and easy disposal.

Lithium/carbon monofluoride was one of the first commercially available lithium batteries and has been used in consumer and military applications. This chemistry has one of the highest theoretical gravimetric energy densities of any of the lithium/solid cathode couples (approximately 2260 Wh/kg). It has a practical gravimetric energy density of 660 Wh/kg and a volumetric energy density of 1000 Wh/l. The low rate capability has limited the use of this system to low or moderate rate applications. While the battery has a very good safety record, it has not been available in sizes larger than DD-size.

This study was initiated for several reasons. There is a growing interest in determining the usefulness of this chemistry as a replacement for power sources presently used in mines and surveillance hardware. For these applications, it must be able to perform over a wide temperature range. In addition, the rate limitation has not been adequately addressed in the literature and the discharge mechanism is not well understood.

The initial investigation presented in this report was to determine the temperature range for commercially available lithium/carbon monofluoride batteries. Impedance spectroscopy was applied in this study in an effort to provide insight into the rate limitation and the discharge mechanism. There has been considerable disagreement in the literature over the actual mechanism.<sup>1,2,3</sup> The simplest mechanism provided by Linden<sup>3</sup> suggests that the carbon monofluoride is reduced, resulting in carbon and fluoride ions. Others believe that a lithium ion intercalates into the carbon monofluoride structure, forming a ternary compound which is reduced and subsequently decomposes to form carbon and lithium fluoride.

While the limited scope of this investigation cannot entirely clarify the mechanism, the impedance study does provide insight and direction for additional study.

### Experimental

#### Cell Construction

The lithium/carbon monofluoride batteries, Model BR-C, were manufactured by Panasonic and purchased from Digi-key Corporation. They were used within about six months of purchase. The actual date of manufacture is not known. The batteries were cylindrical, spirally wound with a diameter of 26.0mm and a height of 50.0mm. Various electrolytes have been used in these batteries, including lithium hexafluorarsenate in dimethyl sulfite, lithium tetrafluoroborate in butyrolactone, tetrahydrofuran, or propylene carbonate and dimethoxyethane. The electrolyte/solvent system used here

was lithium tetrafluoroborate in butyrolactone. The separator is a polyolefin non-woven cloth like polypropylene which is sealed over the cathode with a tab placed in the center of the cathode. In the construction, the anode and cathode sandwich the separator. Panasonic lists the nominal capacity of these batteries as 5Ah and the nominal voltage as 3.0 volts; however, the average open circuit voltage measured for the batteries tested was 3.36 volts. One battery was disassembled and found to have a cathode dimension of 3.75 cm x 28.1 cm yielding an area of 105.4 cm<sup>2</sup> per side.

### **Test Equipment**

The batteries were discharged (Tenny Engineering Inc., Union, NJ) under constant load conditions. Environmental chambers were used to maintain temperature control. Sets consisting of three batteries were discharged at four different temperatures, -20°C, 0°C, 25°C and 70°C, and two different loads, 5 and 50 ohms. The instrumentation used for the constant load discharge was designed, built and programmed at NSWCCD. The load was applied using computer controlled relays with contact resistances of less than a milliohm. Data was acquired with a Keithly Metrabyte DAS1600 data acquisition board. The controlling program allowed for voltage set points and load selection.

AC Impedance measurements were made with a Solartron 1260 Gain-Phase Analyzer used in conjunction with an EG&G PARC Model 273A Potentiostat. The potentiostat was used in a two-terminal mode with the reference electrode lead attached directly to the auxiliary electrode lead. All open circuit measurements were made using the electrometer of the potentiostat. All impedance measurements were made at open circuit with a 1mV amplitude sinusoidal perturbation waveform.

### **Cycling and AC Impedance Procedures**

Prior to discharge at the selected load and temperature, impedance measurements were made on all fresh batteries at open circuit and room temperature. The sets were placed in the Tenny Chambers and allowed to equilibrate at the selected temperature for 24 hours. All batteries were discharged to 0.05 volts to obtain the maximum capacity. The sampling rate was one second for all data acquisition. Batteries that had completely discharged, were allowed to stand at room temperature and open circuit for at least 24 hours prior to making impedance measurements. The batteries were allowed to stand at room temperature for another 30 days after which another impedance measurement was made on each battery. The stand time after discharge was selected to allow the batteries to return to a reproducible equilibrium position. The thirty-day rest period was selected to determine what relaxation occurs, if any, in the batteries when allowed to stand.

### **Results and Discussion**

The discharge protocol used in this investigation did not represent any specific naval application. It was intended to stress the batteries over extreme temperature conditions. Commercial batteries were chosen to determine the capabilities of an available product. This approach minimizes development cost and also identifies areas for improvement to existing systems or new development.



The discharge rates were only moderate; however, the discharge temperatures, in conjunction with the moderate discharge rates, were expected to provide adequate insight into the capabilities of this chemistry. Impedance spectroscopy was used to probe the discharge mechanism and to better understand the apparent high rate limitation found in this chemistry.

### Discharge Behavior

Figures 1 through 4 show the voltage vs. time curves resulting from the discharge of four sets of three batteries at temperatures of 70°C, 25°C, 0°C and -20°C and a load of 50 ohms. Curves for batteries discharged over the same temperature range at 5 ohms are shown in Figures 5 through 8. The figures show the discharge curves for all of the batteries within a set are identical.

The voltage plateaus obtained under each of the discharge conditions were relatively flat. In Figure 7, there is evidence of two plateaus; but that was not observed in any of the other discharge curves. The literature suggested that two plateaus may be observed.<sup>1</sup> The first plateau is believed to be due to the  $\text{CF}_x$  electrochemical reaction and the second is due to the electrolyte reduction. This behavior was not observed for any of the batteries discharged in this study, except those discharged at 0°C with a 5-ohm load. There are visible shoulders on the falling portion of the discharge curve for most of the discharge conditions. The reason for this is not clear, although they could be the electrolyte reduction waves suggested in the literature. In the -20°C discharges at both rates, there is an unexplained increase in the voltage below 0.5 volts. Further, the voltage does not drop off sharply at that temperature, but continues to decrease very slowly for considerably longer than at higher temperatures. The reason for the longer discharge time at low temperature is not obvious but may be due to a multistep mechanism or the viscous nature of the solvent at that temperature.

The average plateau voltage and the average capacity down to a voltage cut-off of 1.8 volts is tabulated for each battery in Table 1.

**Table 1.** Average Plateau Voltage and Average Capacity.

Load Resistor (ohms)	Temperature (°C)	Average Plateau Voltage (V)	Average Capacity @1.8 volts (Ah)
50	70	2.74	6.14
	25	2.54	5.69
	0	2.33	4.72
	-20	2.1	4.18
5	70	2.53	5.22
	25	2.26	4.61
	0	2.05	2.97
	-20	1.75	0.74

Note: The voltages and capacities result from the average of three batteries at each condition

The nominal capacity listed by the manufacture (5Ah) was obtained for the batteries discharged with the 50-ohm load at all but the lowest temperature. Batteries discharged with the 5 ohm load yield the nominal capacity for 70°C and 25°C, but fell

off sharply at the lower temperatures. The capacity at -20°C was only 15% of the nominal capacity.

Under all of the discharge conditions, except those resulting in the discharge curves shown in Figure 1 (temperature = 70°C and load = 50 ohms), there is a sharp voltage drop at the beginning of the discharge followed by a very long rise in voltage to the nominal load voltage. This recovery time is inversely proportional to discharge rate. Looking at any of the discharge curves, it is noted that the recovery times for the batteries discharged at 50 ohms are approximately an order of magnitude longer than for the batteries discharged at 5 ohms at the same temperature. The recovery time increases with increasing temperature, reaching a maximum between 0°C and 25°C, and decreasing as temperature is increased above 25°C. If the discharge data is normalized for the load resistance, the 50-ohm load discharge still results in a more drawn out recovery.

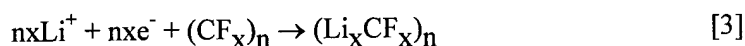
This behavior at the beginning of the discharge is consistent with the fact that carbon monofluoride (CF<sub>x</sub>)<sub>n</sub> has a high electrical resistance. To lower the internal resistance, it is normal practice to include up to 13w/o carbon with the carbon monofluoride. The final products of the discharge are lithium fluoride (LiF) and amorphous carbon as shown below.



As the discharge proceeds, the production of active carbon reduces the internal resistance, resulting in a rise in voltage. During the discharge, LiF is also produced and eventually the beneficial effects of the carbon produced are outweighed by the deposition of LiF in the pores of the cathode. LiF is resistive and should result in a drop in conductivity of the cathode. The deposition of LiF should also affect the diffusion of lithium ions into the cathode, resulting in cell failure. The discharge curves resulting from the 50-ohm discharge demonstrate a normal fall-off in capacity with rate, suggesting that the deposition of LiF under those conditions does not result in capacity loss. It is likely that the LiF is the reason for the extended recovery time noted when the discharge data was normalized for the load resistance. Even at -20°C, the resulting capacity is 84% of the nominal 5Ah. The same cannot be said for the batteries discharged with the 5 ohm load. The discharge at 70°C and 25°C show normal loss in capacity, but the discharges at 0°C and -20°C show a dramatic loss in capacity. At higher rates of discharge, the electron transfer reaction happens closer to the surface, that is, the reaction does not occur very deeply in the pores of the cathode. As a result, the LiF produced is concentrated at the surface and might be expected to interfere with diffusion of the lithium ion into the cathode. Limiting the diffusion of lithium ions to areas near the surface and not allowing diffusion into the pores will isolate the carbon monofluoride deep in the pores leaving it unreacted. This effect will be in addition to the increased viscosity of the solvent which will also act to decrease the diffusion of lithium into the cathode. The combined effect would be expected to cause the dramatic loss in observed capacity.

The relationship between temperature and the noted recovery time is more difficult to understand than the relationship between discharge rate and recovery time. A

multistep reaction mechanism has been proposed in the literature<sup>1,2</sup> to account for the difference in the actual cell potential of 3.3 volts and the theoretical voltage of 4.57 volts. The formation of a ternary compound of lithium, fluoride and carbon has been proposed (Equation [3] and [4]).



If the ternary compound is more conductive than the carbon monofluoride, then the production of that compound, along with any carbon, could be used to explain the increase in cell voltage which was earlier attributed solely to carbon. Assuming that the decomposition reaction is slow, at lower temperatures the production of LiF would be decreased. The fact that the recovery time increases with temperature up to approximately 25°C and then decreases again is not completely explained by the change in the rate of LiF production. It is possible that there is a change in morphology of the LiF which decreases the negative effects at higher temperature. Another possible explanation would be to recall that the viscosity of the solvent is high and at colder temperatures will get higher. As a result, one would expect the electron transfer reaction to not penetrate very far into the porous structure. This is similar to the argument used before to explain the dramatic decrease in capacity at high rates and low temperatures. Further, discharge data supports the assumption that the LiF does not increase the resistance of the cathode significantly early in the discharge. It can then be expected that the recovery time will be shorter at lower temperature. As the temperature is increased, the reaction penetrates into the porous structure producing more carbon and more LiF. As previously noted, the LiF results in a slight increase in the recovery time, most likely by inhibiting diffusion. Finally, at high temperature, the reaction penetrates deeply into the pores, producing a lot of carbon and LiF. However, it is possible that at the higher temperatures, the LiF is more soluble or does not adsorb as strongly on the carbon surface, again decreasing the recovery time. This is an area where more work is required.

Following the completed discharge, the batteries were removed from the environmental chamber and allowed to relax at room temperature for at least 24 hours. This time was required to ensure that the batteries had come to an electrochemical equilibrium, as well as a constant temperature. Except for batteries tested at the lowest temperature, the units returned to room temperature in ten to twenty minutes. No temperature excursions were noted other than normal cooling. The batteries discharged at -20°C underwent a noticeably rapid temperature rise when allowed to stand at room temperature. The temperature change was not measured quantitatively, but the batteries were hot to the touch. After approximately ten to fifteen minutes, the temperature of the batteries began to return to room temperature. The total cooling time for these batteries may have been as long as an hour. This behavior may result from decomposition of the ternary compound discussed above. However, simply increasing the rate of the

decomposition reaction would not explain the heat released. This dramatic temperature change raises some safety concerns. There are applications which would require many batteries to be housed in closed containers and operated at low temperatures. If there was a temperature rise from several batteries under those conditions, the possibility for venting or fire increases. This is also an area which should be further investigated.

### Impedance Spectroscopy

The impedance measurements made on all of the batteries prior to discharge resulted in complex plane plots which were nearly identical. A representative sample, shown in Figure 9, demonstrates a single, slightly depressed, dispersion. The rising tail at low frequency is a result of the porous nature of the cathode.<sup>5-7</sup> The semicircular portion of the curve is due almost entirely to the lithium anode and the polymer film which forms on the lithium surface as a result of interaction with the solvent.<sup>5, 8, 9</sup> There may be a slight contribution from the cathode in the depressed semicircle, but that contribution will be small. The rising tail provides the only information about the cathode available in the impedance measurement of a fresh lithium battery.<sup>5</sup> In addition to the distortions of the dispersion curves due to the rough and coated lithium surfaces and porous nature of the cathode, there may be an inductive effect due to the spirally wound construction of the batteries.<sup>10</sup>

After complete discharge, another impedance measurement was taken on each battery. The shape of the resulting complex plane plots, while quite reproducible between batteries in a particular set, were found to be very dependent on the temperature and rate used to discharge the batteries. This reproducibility suggests that the quality assurance in the manufacturing of these batteries is quite good. When the batteries were allowed to rest at open circuit for about 30 days, the resulting complex plane plots were notably not as reproducible and in some cases, the series resistance measured at high frequency was rather large.

The dispersions observed for the low rate discharge at both 70°C and 25°C (Figure 10) are typical of systems in which the cathode is a porous structure and leads to a reflective boundary behavior. The electrical circuit which models this behavior is an unterminated transmission line as illustrated in Figure 11.<sup>4</sup>

The overall impedance of both dispersions is almost two orders of magnitude greater than that observed for the fresh batteries. It is also interesting to note that the dispersions for both temperatures show a high frequency Warburg-like behavior, suggesting that the cathode process is entirely diffusion limited. The large impedance is due to the deposition of LiF deep in the pores of the cathode. The high frequency semicircle indicates that some LiF was deposited on the surface and the rest is in the pores. This is reflected by the low frequency constant phase response indicated by the straight line. The lower slope of that low frequency is expected, since, at higher temperatures, more LiF is deposited deeper in the pore structure. Figure 12 shows the dispersion for a low rate discharge at 0°C. The tail at low frequency has almost disappeared and two clear time constants are observed. The higher frequency time constant is most likely due to the LiF film formation. This suggests that, at lower temperatures, the electrochemical process does not penetrate the cathode very far and deposits a greater amount of LiF on or near the surface rather than in the pore structure. The loss of the low frequency tail implies that the pore structure is much less accessible and therefore does not appear in the spectrum. Further support for this interpretation is

seen in Figure 13, which shows the dispersion obtained for a low rate discharge at  $-20^{\circ}\text{C}$ . There are two time constants observed in that figure and no low frequency tail. It is further observed that the overall impedance for that dispersion is only 25% of the overall impedance observed at the other three temperatures. The previous spectra showed real resistances which were three times greater than that observed at  $-20^{\circ}\text{C}$ . The decrease in the overall impedance is not due to less LiF, since the capacity removed during that discharge was 85% of the nominal capacity. That would indicate that the amount of LiF produced was only 15% less than that produced from the other discharge conditions. It must be assumed that the morphology of the LiF film is very different and less resistive, or most of the LiF produced fell off of the surface.

Figures 14 through 17 show the dispersions obtained for batteries discharged under a 5-ohm load. The complex plane plot for the battery discharged at  $70^{\circ}\text{C}$  shows no low frequency tail and the high overall impedance is the same as that observed for the low rate discharge dispersions. The dispersions observed at  $25^{\circ}\text{C}$  is quite similar in shape and impedance to that obtained at low rate and  $-20^{\circ}\text{C}$ . The same argument applied to describe the results of the low rate discharge are most likely applicable here as well. It should be noted that the overall impedance decreases with decreasing temperature, a result not observed in the low rate discharge. The dispersion obtained from the batteries discharged at  $0^{\circ}\text{C}$  and  $-20^{\circ}\text{C}$  (Figure 16 and 17 respectively) looks very similar to the fresh battery without a low frequency tail. This result is consistent with the very low capacity obtained for that discharge. Any LiF formed would be right at the cathode surface, completely blocking the pore structure of the cathode. That blocking effect along with the lowered diffusion, due to the increased viscosity of the solvent, serve to isolate most of the cathode from reaction and result in battery failure.

Attempts to fit these dispersion curves has not been successful. It is expected that the cylindrical, spirally wrapped construction results in very poor current distribution within the battery during impedance measurements. This could be tested by opening a battery and performing an impedance measurement with the electrodes in a prismatic configuration.

The dispersion curves obtained after all of the batteries were allowed to stand at open circuit for a least thirty days at room temperature, were similar in shape to those obtained after discharge. Many of the dispersion curves showed an increased series resistance and in most cases, an increase in the overall impedance. This result may be explained by considering that the LiF layer will digest after standing and may become more crystalline and therefore even more resistive. It is interesting to note that the dispersion obtained for the battery discharged at  $-20^{\circ}\text{C}$  and 5 ohms nearly returned to the state of the fresh battery after standing. This observation further supports the development of a passive layer right at the surface which dissolves on standing. Presumably this battery could be discharged again since very little of the total capacity was used in the initial discharge. The increase in high frequency series resistance could represent corrosion of the current collectors.

### Conclusions

The performance of the Panasonic C-size carbon monofluoride batteries at room temperature and above was quite good. The voltage plateaus were flat but did show some sensitivity to temperature. The reproducibility of the battery discharge behavior within each set of batteries was excellent suggesting that the manufacturing procedures

used by Panasonic were very good. Even the impedance measurements showed excellent reproducibility. Impedance measurements are very sensitive to the battery construction. It is clear from the discharge behavior of these batteries, as produced, that they do not perform well at low temperatures. That low temperature behavior is far worse at higher discharge rates. The load voltage range for the 50-ohm discharge was 2.7 to 2.2 volts while it was 2.6 to 1.8 for the discharges with a 5-ohm load. The load voltages under both discharge conditions could be improved if a solvent with a lower viscosity and better temperature properties was used.

The production of LiF and subsequent deposition of that material on the surface and in the pores did not grossly affect the capacities available from the batteries except for the 5 ohm load discharges at low temperatures.

The complex plane results confirm the production of the LiF near the surface at high rates of discharge and low temperatures, but do not provide more detailed insight into the mechanism. It would be more useful to acquire the impedance spectra at many points during the discharge. Further, inability to fit the impedance data made drawing more complete conclusions difficult.

The discharge of these batteries at temperatures of 0°C to 70°C down to approximately 0.1 volts at both discharge rates resulted in no venting or other safety concerns. The unexplained temperature excursions noted for batteries discharged at -20°C at both rates is of concern. More investigations are necessary to quantify that event and determine whether the temperature excursions occur at temperatures between -20°C and 0°C.

### Recommendations

A better understanding of the discharge mechanism could be obtained if the impedance data were acquired throughout the discharge. All of the dynamic information from this investigation was lost because of the necessity of allowing the batteries to come to steady state. Future work should include dynamic impedance measurements. This would require that at each selected voltage, the batteries are potentiostatically held at the stopping voltage so that the impedance measurements reflect the non-steady state condition within the battery. These types of measurements will provide far more insight into the mechanism than can be obtained from measurements made at equilibrium.

The effects of the spirally wound construction could be accounted for if a prismatic version of the  $\text{LiCF}_x$  battery were constructed and used for the impedance measurements. Such a laboratory cell would allow the use of reference electrodes which would provide information about the anode and cathode contributions to the total impedance.

The temperature rise observed after the discharge at -20°C should be more carefully investigated. Cells with thermocouples on the cases should be discharged and allowed to return to room temperature. The changes in temperature could be measured leading to a better understanding of that phenomenon. Impedance measurements could be made on the batteries while they are returning to room temperature. This data may provide additional insight into the mechanism responsible for the temperature excursions.

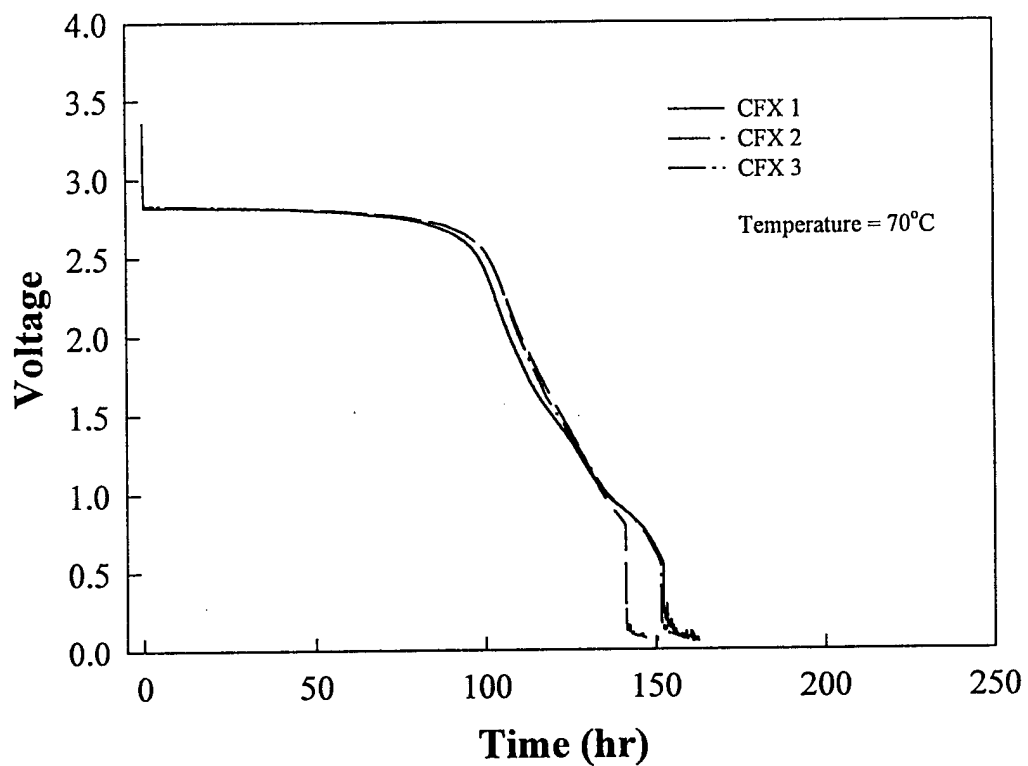


Figure 1. Discharge Curve for Three Cells under a Load of 50 ohms at 70°C.

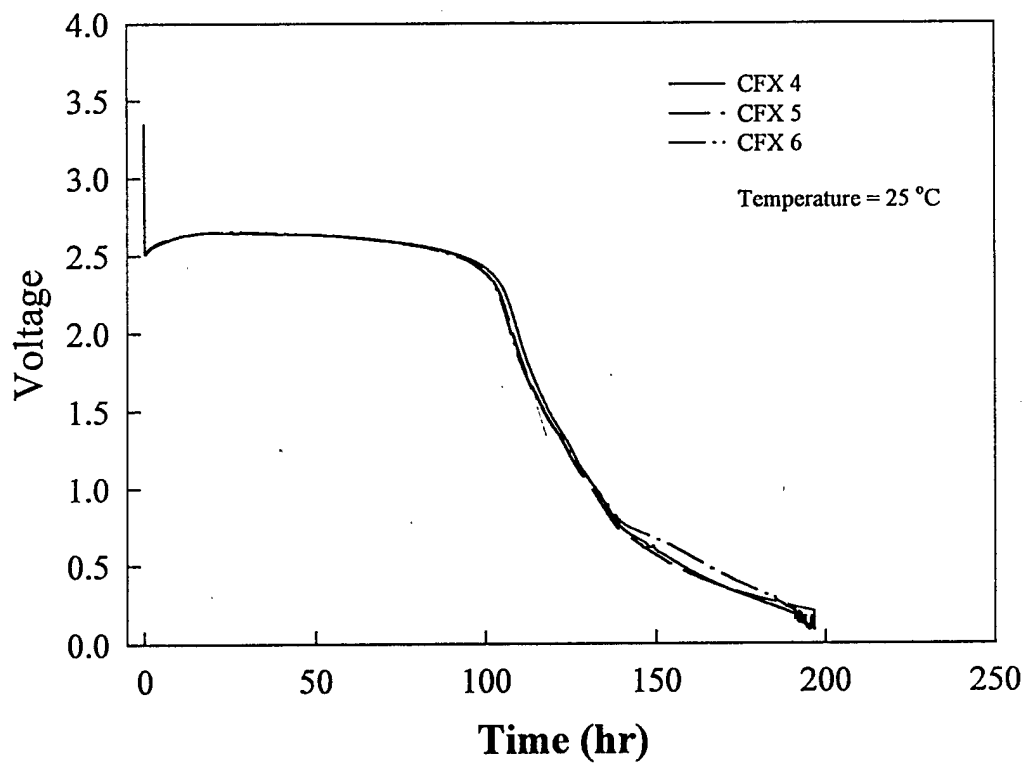


Figure 2. Discharge Curve for Three Cells under a Load of 50 ohms at 25°C.

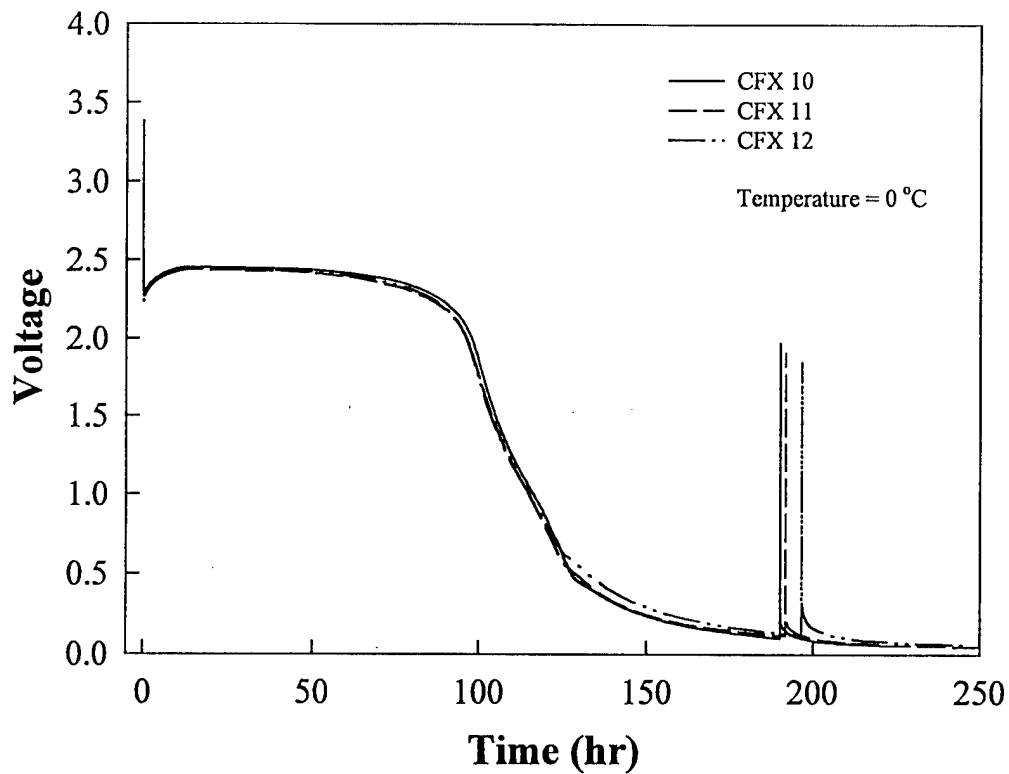


Figure 3. Discharge Curve for Three Cells under a Load of 50 ohms at 0°C.

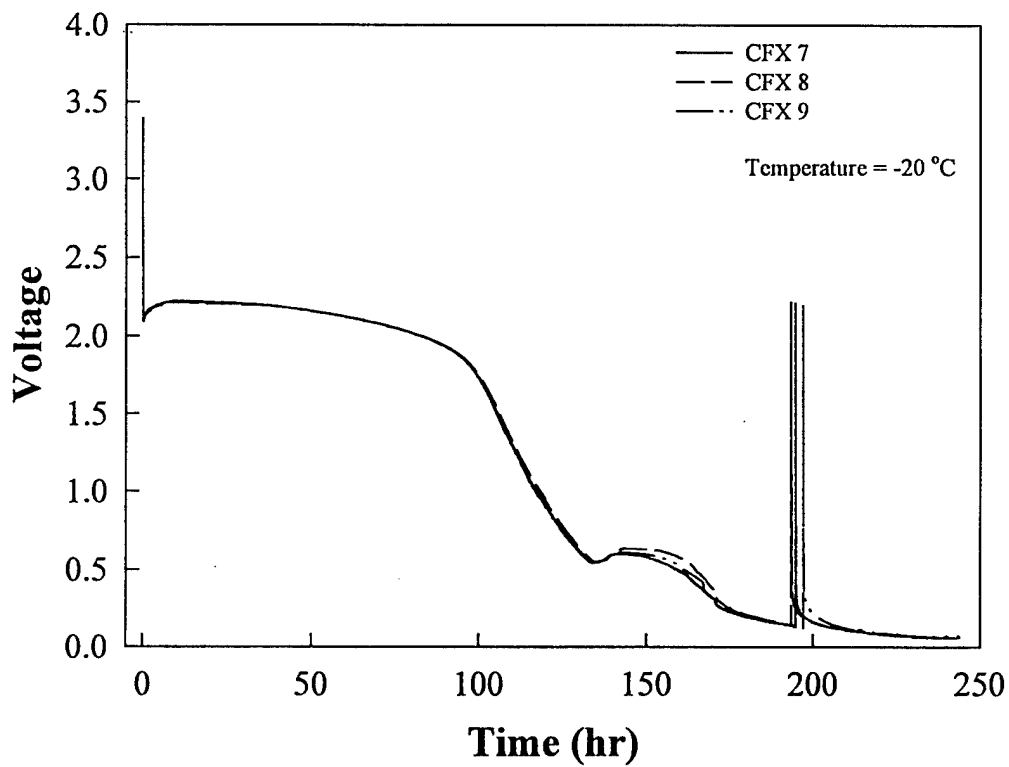


Figure 4. Discharge Curve for Three Cells under a Load of 50 ohms at -20°C.



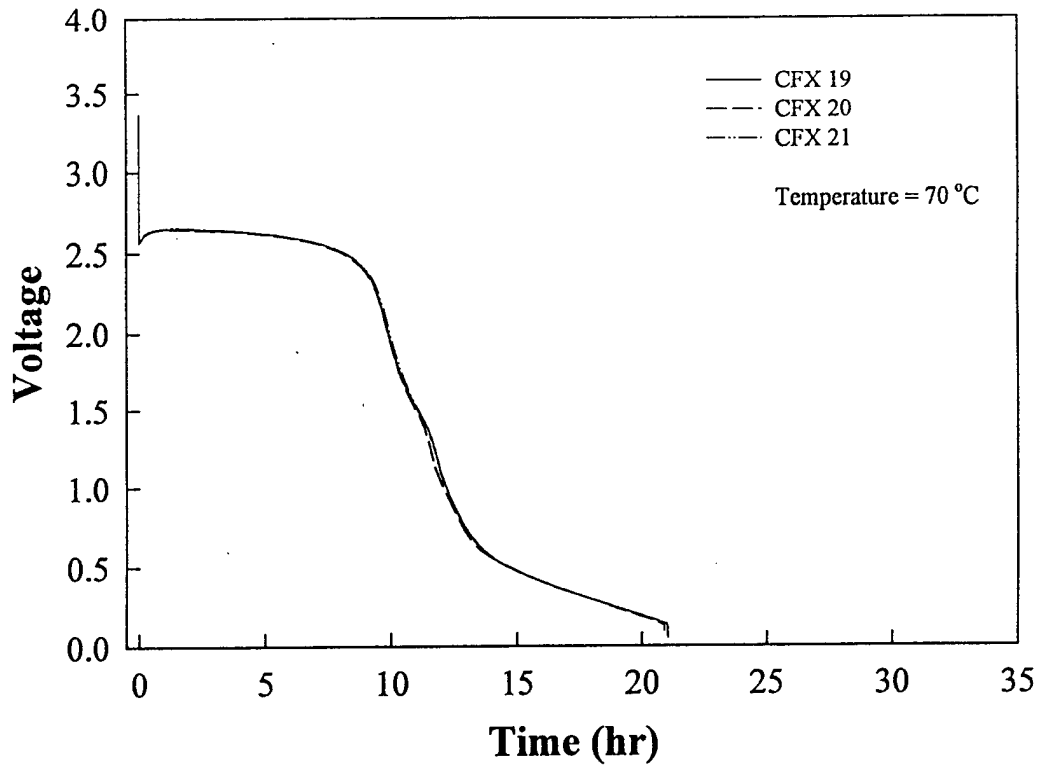


Figure 5. Discharge Curve for Three Cells under a Load of 5 ohms at 70°C.

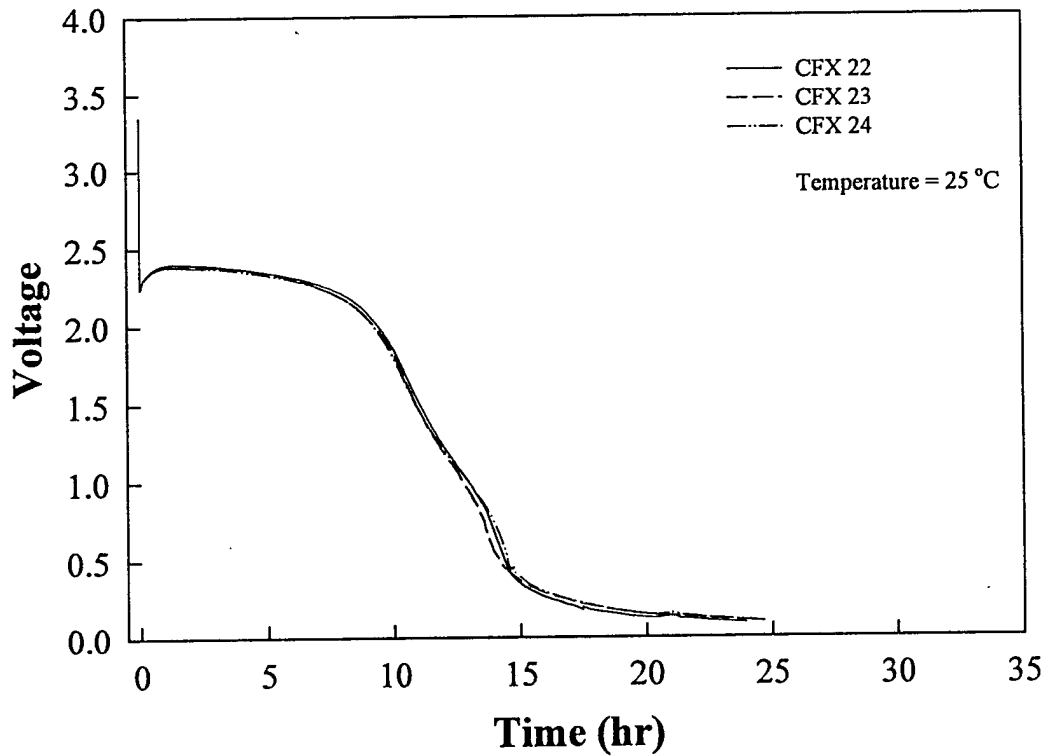


Figure 6. Discharge Curve for Three Cells under a Load of 5 ohms at 25°C.

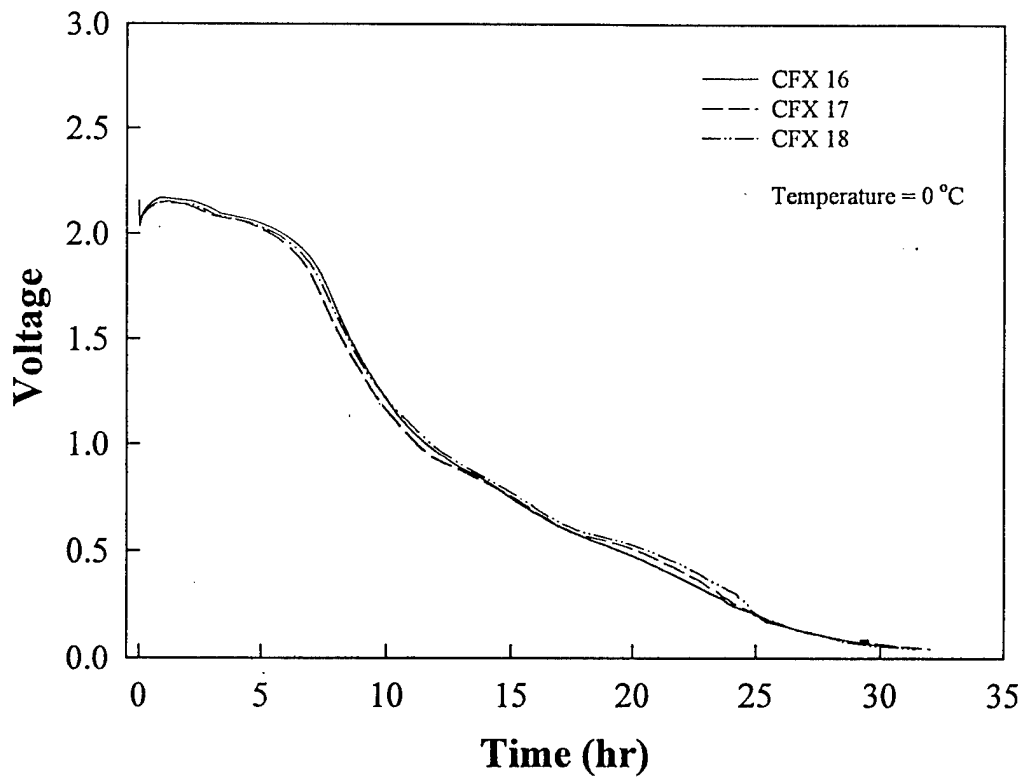


Figure 7. Discharge Curve for Three Cells under a Load of 5 ohms at 0°C.

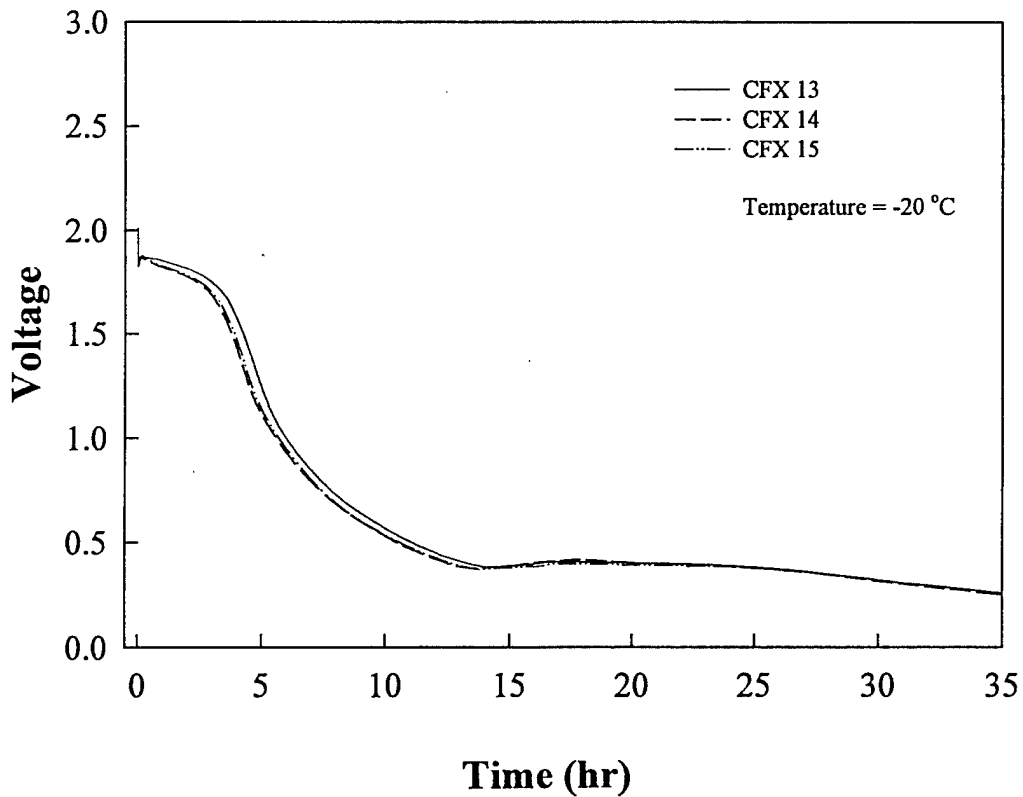


Figure 8. Discharge Curve for Three Cells under a Load of 5 ohms at -20°C.

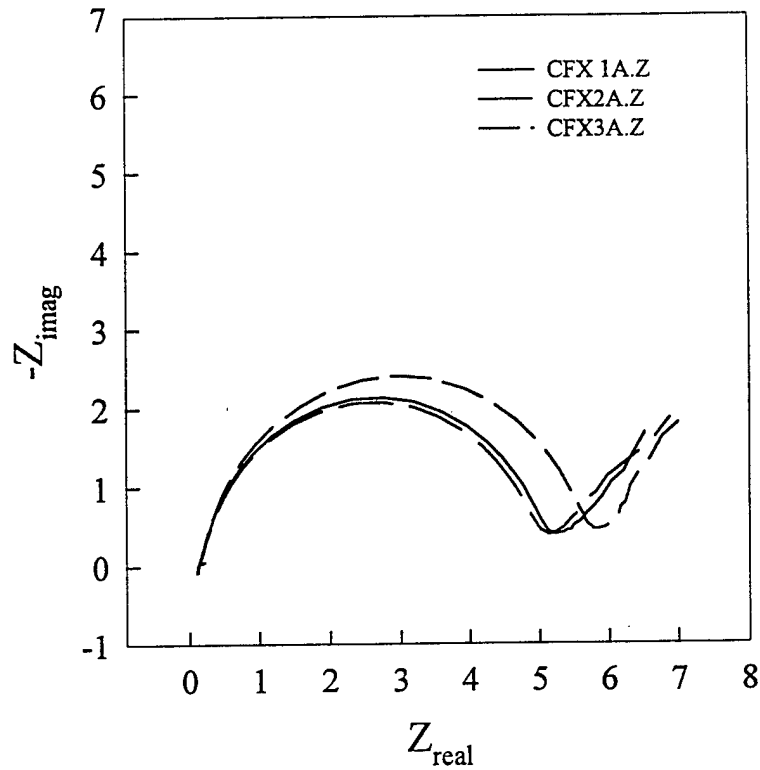


Figure 9. Complex Plane Impedance Spectra for Three Fresh Cells Prior to Discharge.

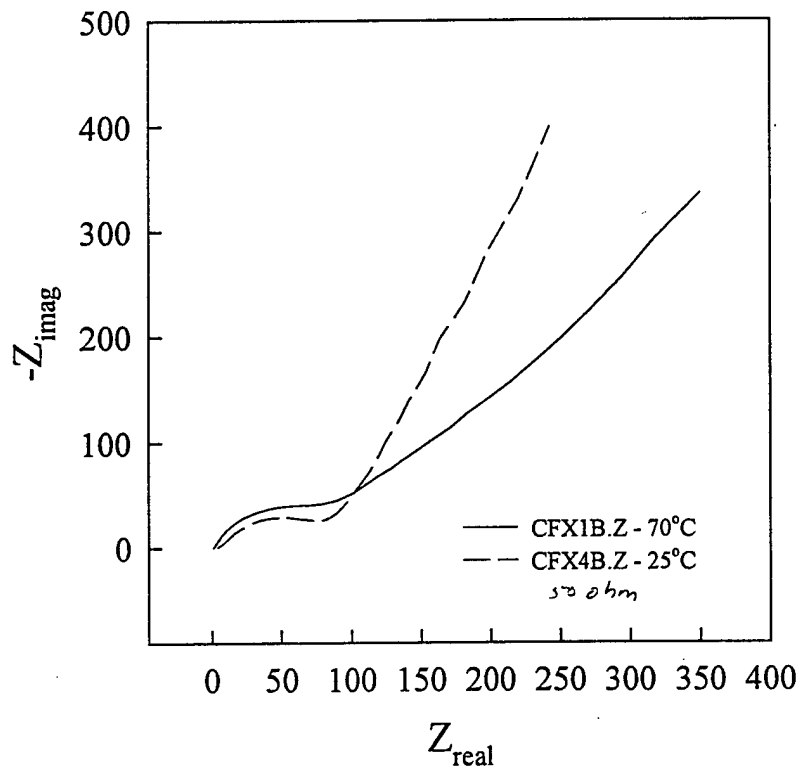
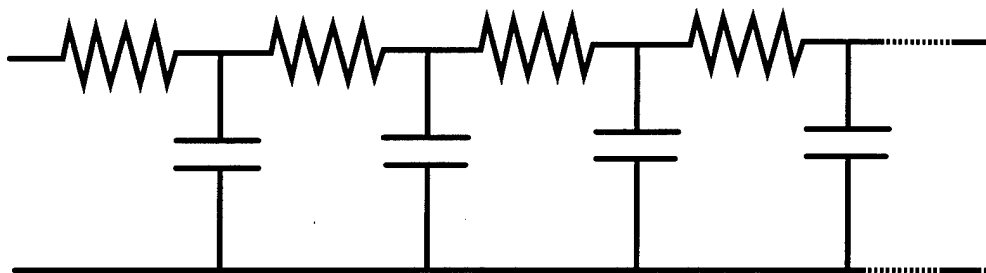
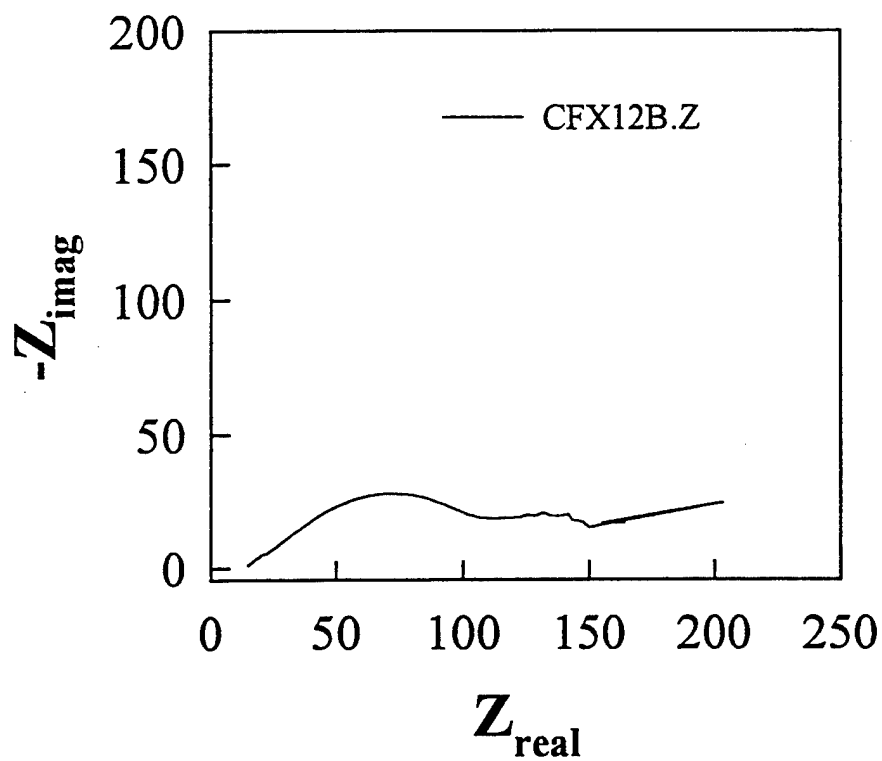


Figure 10. Complex Plane Impedance Spectra for Two Cells Completely Discharged with a 50-ohm Load



**Figure 11.** Equivalent Circuit Used to Model a Diffusional Impedance and the Observed Impedance within a Porous Structure.



**Figure 12.** Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 50 ohms at 0°C.

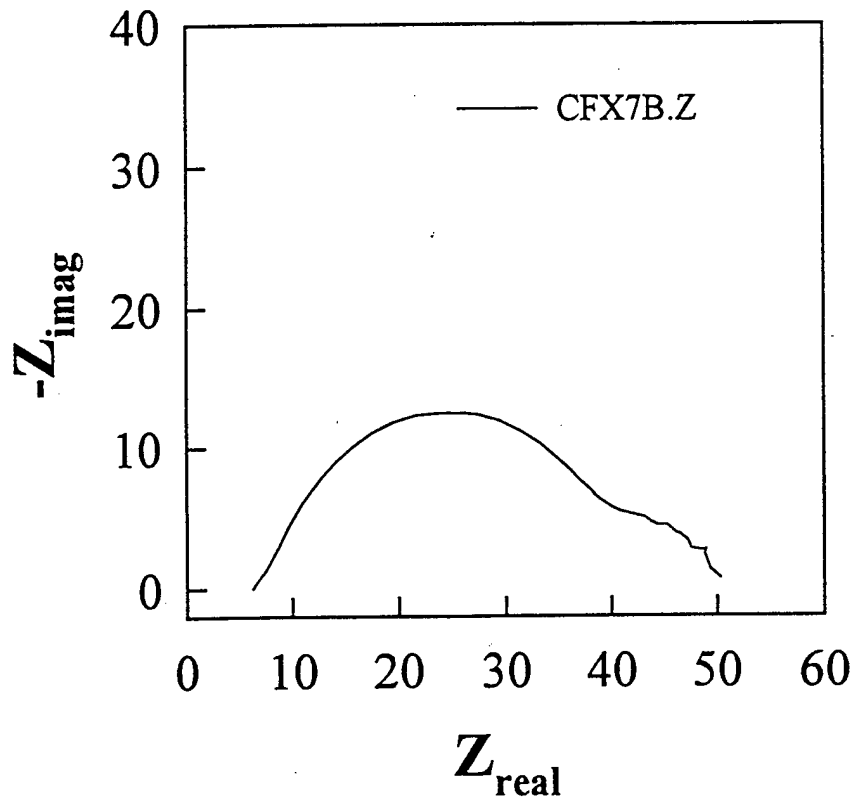


Figure 13. Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 50 ohms at -20°C.

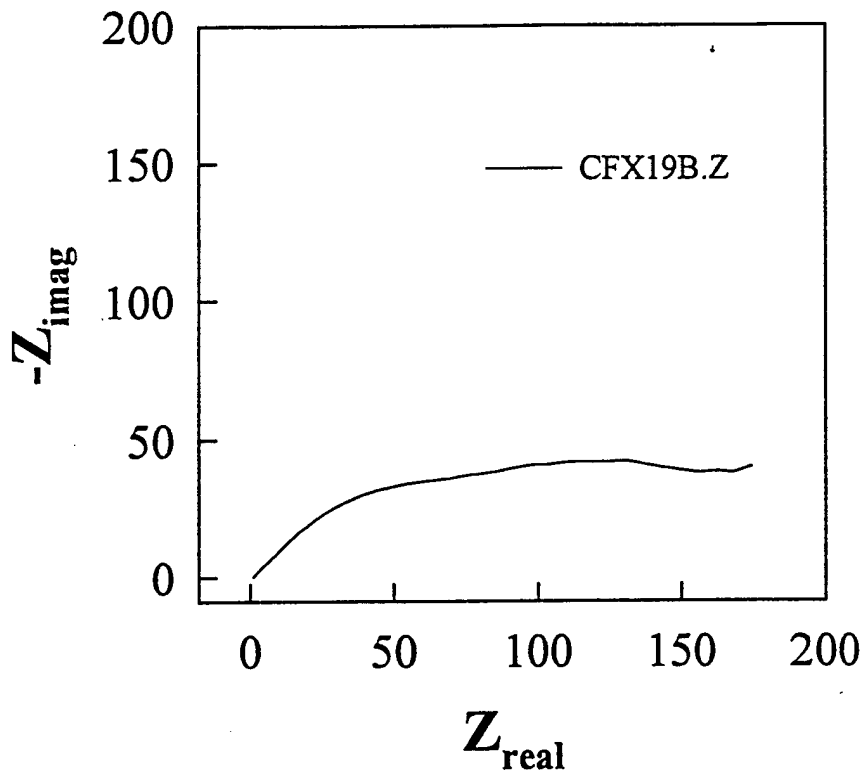
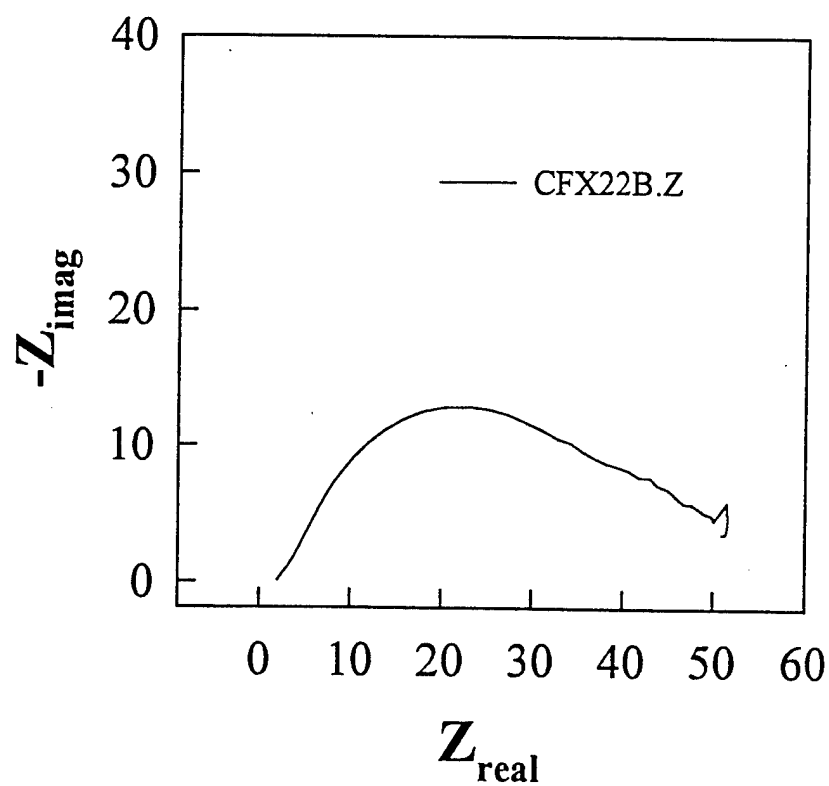
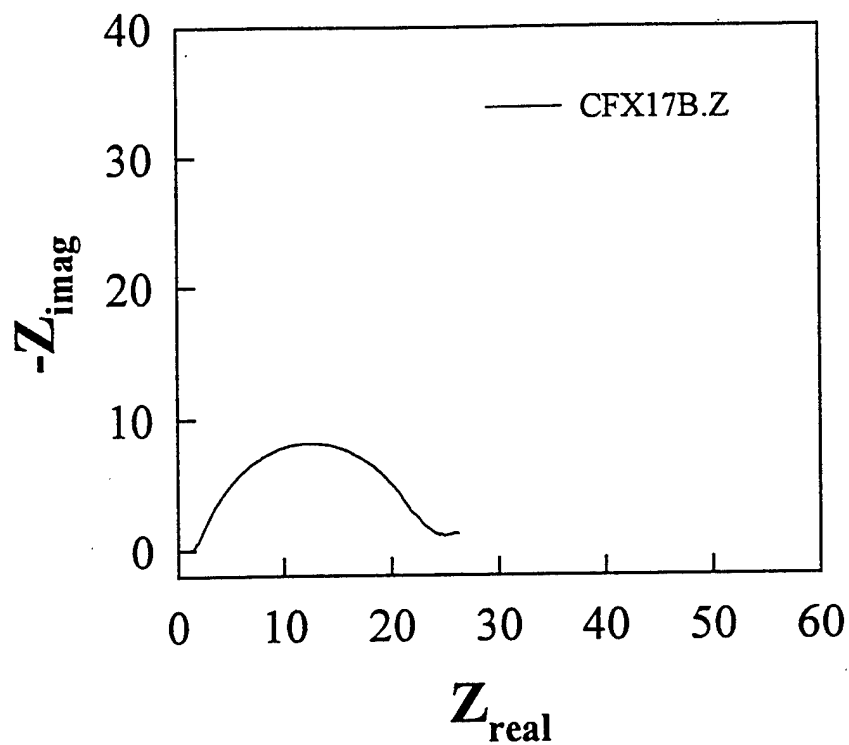


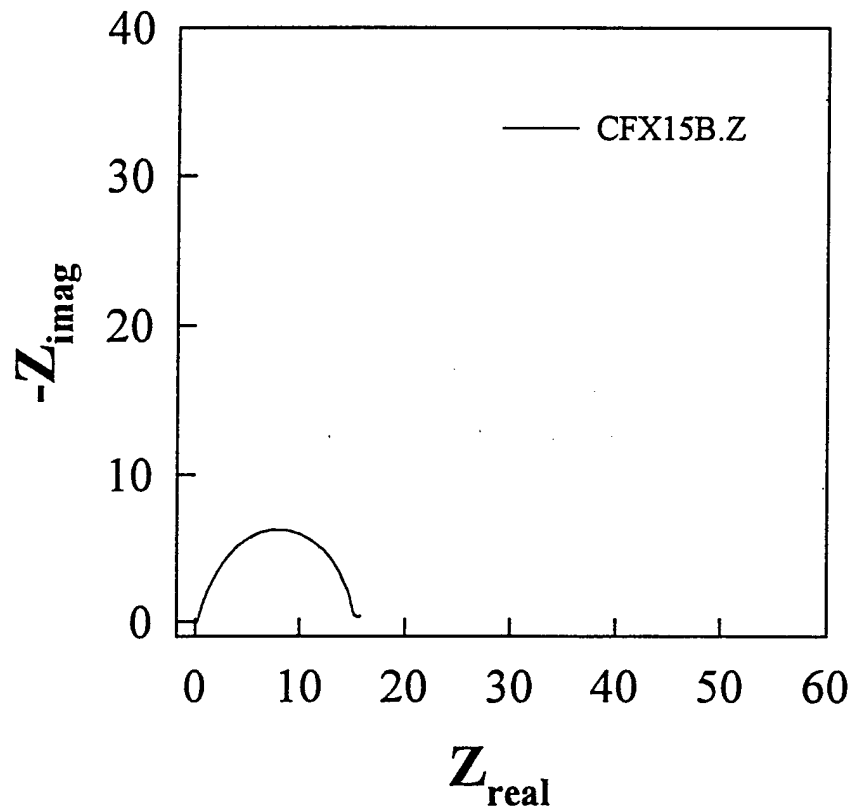
Figure 14. Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 70°C.



**Figure 15.** Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 25°C.



**Figure 16.** Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at 0°C.



**Figure 17.** Complex Plane Impedance Spectrum for a Cell Fully Discharged under a Load of 5 ohms at  $-20^{\circ}\text{C}$ .

### References

1. Pasquariello, D.M., E.B. Willstaedt and K.M. Abraham, *Proceedings of the Symposium on Primary and Secondary Lithium Batteries*, Vol. 91-3 (edited by K.M. Abraham and M. Salomon)
2. Watanabe, N., R. Hagiwara, T. Nakajima, H. Touhara, and K. Ueno, *Electrochimica Acta*, Vol. 27, p.1615 (1982).
3. *Handbook of Batteries*, 2nd Edition, David Linden editor, 14.59-14.69, McGraw-Hill, Inc., (1995).
4. Macdonald, J. R., *Impedance Spectroscopy-Emphasizing Solid Materials and Systems*, John Wiley & Sons, p. 59-60 (1987).
5. Zoski, G., P. Smith, S. James and T. Murphy, *Progress in Batteries & Battery Materials*, Vol. 11, pp. 188-202 (1992).
6. Raistrick, I.D., *Electrochimica Acta*, Vol. 35, pp. 1579-1586 (1990).
7. DeLevie, R., *Advances in Electrochemistry and Electrochemical Engineering*, P. Delahay and C.T.Tobias, editors, Vol 6, p. 329, Interscience, New York (1967).
8. Montesperelli, G., P. Nunziante, M. Pasquali, and G. Pistoia, *Solid State Ionics*, Vol. 37, pp. 149-156 (1990)
9. Thevenin, J., *Journal of Power Sources*, Vol. 14, pp. 45-52 (1985)
10. Laman, F.C., M.W. Matsen, and J.A. R. Stiles, *J. Electrochem. Soc.*, Vol. 133, p. 2141, (1986).



## DISTRIBUTION

	<u>Copies</u>		<u>Copies</u>
<b>DOD ACTIVITIES (CONUS)</b>		ATTN D GUERRINO	1
		NAVAL ELECTRONICS SYSTEMS	
ATTN ONR 321 (D JOHNSON)	1	SECURITY CENTER	
ONR 322 (T GOLDSBERRY)	1	3801 NEBRASKA AVE	
ONR 322 (K DIAL)	1	WASHINGTON DC 20390-5270	
ONR 322 (R VARLEY)	1		
ONR 322 (S LITTLEFIELD)	1	ATTN PMA 264 (E BENSON)	1
ONR 331 (R DEMARCO)	1	PMA 264 (R DAVIS)	1
ONR 331 (R NOWAK)	1	PMA 264 (T TAMPA)	1
ONR 333 (S LEKOUDIS)	1	COMMANDER	
ONR 333 (J FEIN)	1	PROGRAM EXECUTIVE OFFICE	
ONR 333 (D STEIGER)	1	AIR ASW ASSAULT AND SPECIAL	
OFFICE OF NAVAL RESEARCH BT	1	MISSION PROGRAMS	
800 N QUINCY STREET		1421 JEFFERSON DAVIS HWY	
ARLINGTON VA 22217-5660		ARLINGTON VA 22243-5120	
ATTN PMS393	1	ATTN CODE E232	3
PMS403 (C YOUNG)	1	CODE E35	1
PMS407	1	CODE N742 (GIDEP)	1
PMS415G (B KRIESE)	1	COMMANDER	
COMMANDER		NAVAL SURFACE WARFARE CENTER	
NAVAL SEA SYSTEMS COMMAND		DAHLGREN DIVISION	
2531 JEFFERSON DAVIS HWY		17320 DAHLGREN ROAD	
ARLINGTON VA 22242-5160		DAHLGREN VA 22448-5100	
ATTN CODE 633 (L JOHNSON)	1	ATTN L DUBOIS	1
CODE 634 (P BOSS)	1	R ROSENFELD	1
CODE 634 (S SZPAK)	1	ARPA/DSO	
COMMANDER		3701 NORTH FAIRFAX DRIVE	
NAVAL COMMAND CONTROL AND		ARLINGTON VA 22203-1714	
OCEAN SURVEILLANCE CENTER			
SAN DIEGO CA 92512-5000		ATTN CODE 609 (J GUCINSKI)	1
		CODE 609A (W JOHNSON)	1
		COMMANDER	
ATTN SPAWAR OOF/052-2H (F SLIWA)	1	NAVAL SURFACE WARFARE CENTER	
COMMANDER		CRANE DIVISION	
SPACE AND NAVAL WARFARE		300 WEST HIGHWAY 98	
SYSTEMS COMMAND		CRANE IN 47522-5083	
2451 CRYSTAL DRIVE			
ARLINGTON VA 22242-5160			

**DISTRIBUTION (Continued)**

	<u>Copies</u>		<u>Copies</u>
ATTN CODE 804 (S TUCKER)	1	ATTN CODE AFWAL/P00S (R MARSH)	2
CODE 8291 (C EGAN)	1	WRIGHT LABORATORIES	
CODE 8291 (D GOODRICH)	1	AIR FORCE SYSTEMS COMMAND	
CODE 8292 (P DUNN)	1	WRIGHT-PATTERSON AIR FORCE	
COMMANDER		BASE OH 45433-6563	
NAVAL UNDERSEA WARFARE			
CENTER		ATTN H CHRISTOPHER	1
NEWPORT DIVISION		M T BRUNDAGE	1
NEWPORT RI 02841-5047		S GILMAN	1
		E REISS	1
ATTN LIBRARY	1	COMMANDER	
NAVAL TECHNICAL INTELLIGENCE		US ARMY EPSD (ARL)	
CENTER		MAIL CODE AMSRL-EP-PB	
4301 SUITLAND ROAD		FORT MONMOUTH NJ 07703-5601	
WASHINGTON DC 20390			
		ATTN A GOLDBERG	1
ATTN CODE 2310 (E RICHARDS)	1	COMMANDER	
CODE 2330 (G COOPER)	1	US ARMY RESEARCH LABORATORY	
COMMANDER		AMSRL-EP-PC	
NAVAL SURFACE WARFARE CENTER		2800 POWDER MILL ROAD	
DAHLGREN DIVISION		ADELPHI MD 20783-1197	
COASTAL SYSTEMS STATION		DEFENSE TECHNICAL	
6703 WEST HIGHWAY 98		INFORMATION CENTER	
PANAMA CITY FL 32407-7001		8725 JOHN J KINGMAN DR	
		SUITE 0944	
ATTN CODE 714 (K E ROGERS)	1	FT BELVOIR VA 22060-6218	2
NCCOSC RDTE DIV 714			
49590 LASSING RD RM A456		<b>NON-DOD</b>	
SAN DIEGO CA 92152-6161			
		ATTN OTS (T X MAHY)	1
ATTN CODE BMO/ENSE	1	CENTRAL INTELLIGENCE AGENCY	
CODE AFISC/SES	1	WASHINGTON DC 20505	
NORTON AIR FORCE BASE			
NORTON AFB CA 92409		ATTN EE-321 (A LANGREBE)	1
		EE-321 (R A SUTULA)	1
ATTN CODE 8520 (M CERVI)	1	EE-321 (P B DAVIS)	1
CODE 824 (J WOERNER)	1	DEPARTMENT OF ENERGY	
NAVAL SURFACE WARFARE		1000 INDEPENDENCE AVENUE	
CENTER		WASHINGTON DC 20585	
CARDEROCK DIVISION			
ANNAPOLIS LABORATORY		ATTN T C MURPHY	1
3A LEGGETT CIRCLE		IDAHO NATIONAL ENGINEERING	
ANNAPOLIS MD 21401		LABORATORY	
		PO BOX 1625	
		IDAHO FALLS ID 83415-3830	

## DISTRIBUTION (Continued)

	<u>Copies</u>		<u>Copies</u>
ATTN SPACE POWER APPLICA- TIONS BRANCH (CODE 711)	1	ATTN G CRUZE	1
NASA GODDARD SPACE FLIGHT CENTER		K MAUTER	1
GREENBELT ROAD		W BOWDEN	1
GREENBELT MD 20771		A N DEY	1
		F GIBBARD	1
		DURACELL USA	
ATTN CRS-ENR (A ABELL)	1	TECHNICAL SALES MARKETING	
CRS-SPR (F SISSINE)	1	GROUP	
LIBRARY OF CONGRESS		BERKSHIRE INDUSTRIAL PARK	
WASHINGTON DC 20540		BETHEL CT 06801	
ATTN CODE EP5 (B J BRAGG)	1	ATTN LIBRARY	1
NASA JOHNSON SPACE CENTER		POWER CONVERSION INC	
NASA ROAD 1		495 BOULEVARD	
HOUSTON TX 77058		ELMWOOD PARK NJ 07407	
ATTN MS 433 (J GOWDEY)	1	ATTN LIBRARY	1
NASA LANGLEY		DEPT 9350 (R HOLLANDSWORTH)	1
HAMPTON VA 23665		LOCKHEED MISSILES AND SPACE	
		COMPANY INC	
ATTN CODE WDB2 (D SCALLEY)	1	3251 HANOVER STREET	
NOAA DATA BUOY CENTER		PALO ALTO CA 94304	
NSTL STATION MS 39529			
		ATTN DEPT 8144 (V TEOSILO)	1
ATTN N DODDAPANENI	1	LOCKHEED MISSILES AND SPACE	
R GUIDOTTI	1	COMPANY INC	
SANDIA NATIONAL LABORATORIES		PO BOX 3504	
MAILSTOP 0614		SUNNYVALE CA 94088-3504	
ALBUQUERQUE NM 87185-0614			
		ATTN R W RACE	1
ATTN C J KELLY	1	GENERAL ELECTRIC CO	
D P ROLLER	1	MGR ADVANCED K-PROGRAMS	
ALLIANT TECHSYSTEMS		MARKETING	
104 ROCK ROAD		ROOM 2546 OP#2	
HORSHAM PA 19044		100 PLASTICS AVENUE	
		PITTSFIELD MA 01201	
THE CNA CORP		ATTN C SCHLAIKJER	1
4401 FORD AVENUE		BATTERY ENGINEERING INC	
ALEXANDRIA VA 22302-0268	1	1536 HYDE PARK ROAD	
		HYDE PARK MA 02136	
ATTN LIBRARY	1		
R L HIGGINS	1	ATTN D FOUCHARD	1
D SPENCER	1	R REA	1
EAGLE PICHER INDUSTRIES		RAYOVAC CORP	
COUPLES DEPARTMENT		601 RAY O VAC DRIVE	
PO BOX 47		MADISON WI 53711	
JOPLIN MO 64802			

## DISTRIBUTION (Continued)

	<u>Copies</u>		<u>Copies</u>
ATTN F WALSH ECO 20 ASSEMBLY SQUARE DR SOMERVILLE MA 02145	1	ATTN N ISAACS MSA 38 LOVETON CIRCLE SPARKS MD 21152	1
ATTN S SIROIS MS-R354 MITRE CORPORATION BURLINGTON RD BEDFORD MA 01730	1	ATTN R STANIEWICZ SAFT AMERICA 107 BEAVER COURT COCKEYSVILLE MD 21030	1
ATTN T REDDY R SERENYI YARDNEY TECHNICAL PRODUCTS 92 MECHANIC STREET PAWCATUCK CT 02891	1 1	ATTN N SHUSTER WESTINGHOUSE ELECTRICAL POWER SYSTEMS 476 CENTER STREET CHARDON OH 44024	1
ATTN E TAKEUCHI WILSON GREATBATCH LTD 10000 WEHRLE DRIVE CLARENCE NY 14031	1	ATTN B VYAS AT&T BELL LABORATORIES 600 MOUNTAIN AVENUE MURRAY HILL NJ 07974	1
ATTN K M ABRAHAM EIC LABORATORIES INC 111 DOWNEY STREET NORWOOD MA 02062	1	ATTN S MEGAHED RBI CORPORATION 2228 EVERGREEN ROAD MIDDLETON WI 53562	1
ATTN A HIMY J J MCMULLEN ASSOCIATES INC 2341 JEFFERSON DAVIS HIGHWAY ARLINGTON VA 22202	1	ATTN P M NARENDRA MN11-1225 ALLIANT TECHSYSTEMS INC 600 SECOND ST NE HOPKINS MN 55343-8384	1
ATTN D L CHUA H-P LIN MAXPOWER 220 STAHL RD HARLEYSVILLE, PA 19438	1 1	ATTN C W FLEISCHMANN G D ZOSKI ATR 15210 DINO DRIVE BURTONSVILLE MD 20866-1172	2 2
ATTN W EBNER FMC CORP LITHIUM DIV HIGHWAY 161 BOX 795 BESSEMER CITY NC 28016	1		
ATTN G SKELTON HUGHES AIRCRAFT COMPANY UNDERSEA WEAPONS SYSTEMS DIVISION BLDG 618 MS/Q111 PO BOX 3310 FULLERTON CA 92634	1		

**DISTRIBUTION (Continued)**

		<u>Copies</u>		<u>Copies</u>
<b>NSWC CARDEROCK DIVISION</b>		3023	(TIC/WHITE OAK)	1
<b>INTERNAL DISTRIBUTION</b>		3024	(TIC/ANNAPOLIS)	1
		60	(WACKER)	1
011 (CORRADO)	1	601	(MORTON)	1
0112 (DOUGLAS)	1	603	(CAVALLARO)	1
0115 (CAPLAN)	1	68	(MUELLER)	1
0119 (MESSICK)	1	683	(BARNES)	1
3021 (COLEGROVE)	1	683	(P SMITH)	10
3023 (TIC/CARDEROCK)	1	683	(FILES)	40